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HAWAII UNIV HONOLULU DEPT OF PHYSICS AND ASTRONOMY
LOW ENERGY X-RAY AND ELECTRON INTERACTIONS WITHIN MATTER.(U)
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LOW ENERGY X-RAY AND ELECTRON INTERACTIONS
WITHIN MATTER.

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Final Technical Report.

01 July 1974 through 30 Sep 1978

Grant AFOSR-75-2762

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Final Technical Report

Grant AFOSR 75-2762

**LOW ENERGY X-RAY AND ELECTRON INTERACTIONS
WITHIN MATTER**

01 July 1974 through 30 September 1978

→ **TOPICS:**

- I. Introduction--Low Energy X-Ray and Electron Spectroscopy (Directed to the High Temperature Plasma Diagnostics);
 - A. Development of High Efficiency Low Energy X-Ray Spectroscopy,
 - B. Valence-Band and Molecular Orbital Analysis, and
 - C. Development of the Physics and Application of X-Ray Photocathodes.
- II. Research Publications (Published, In Press and In Preparation)
- III. Research Papers Presented at Scientific Meetings by this Principal Investigator on this AFOSR Program
- IV. Appendices

**I. INTRODUCTION--LOW ENERGY X-RAY AND ELECTRON SPECTROSCOPY
(DIRECTED TO THE HIGH TEMPERATURE PLASMA DIAGNOSTICS)**

In the controlled thermonuclear fusion research and in the development of super-radiant x-ray sources, plasma temperatures of greatest current interest are in the one to ten million degree range. These are characterized by their corresponding radiations in the kilovolt and sub-kilovolt region, the low energy x-region. Their spectroscopy can yield information as to temperature, density and temporal history (into the picosecond region). The principal current effort of this AFOSR program

has been in support of this application which is of very considerable present need. This support, however, is basically in our development of the needed sensitive and high efficiency low-energy x-ray and electron spectroscopy. These developments are also being applied at our laboratory and/or collaboratively with other laboratories in other areas as material sciences and x-ray astronomy.

A. Development of High Efficiency Low Energy X-Ray Spectroscopy

Methods and Instruments--In three recent reports [53,55,58] we have presented in detail our "state of the art" approach to sub-kilovolt x-ray spectroscopy based upon an optimized application of long spacing x-ray crystal analyzers of the Langmuir-Blodgett type and as perfected on this AFOSR project. A computerized spectral analysis procedure has been developed [58], the LEX/2, for obtaining the maximum of physical information from typical overlapping low energy x-ray spectra. This program incorporates a built-in program for the calculation of the atomic photoionization cross sections of all elements that are typically involved in self-absorption corrections for the radiation source. The "state of the art" absorption tables for the low energy x-ray region as based upon experimental measurements by the project and by all others that have been reported and upon the best available theory have been parameterized [52,71] for such direct computerized applications.

B. Valence-Band and Molecular Orbital Analysis

As a means of testing and refining these newly developed techniques of low energy x-ray spectroscopy in our laboratory, we are applying these to the characterization of the valence band and molecular orbital states of atomic, molecular and crystalline systems. These studies are based upon the fact that transitions from the valence states into the nearest, relatively sharp inner levels yield low energy x-ray spectra that sensitively portray the characteristics of the outer electronic states. Such information is of considerable importance in the material science area and in providing greatly needed data for the development of the large computer modeling of chemical systems. A new technique has been developed in these studies for the identification and measurement of radiation damage effects upon materials [58]. These studies have been published as based upon the L_{II,III} spectroscopy of sulfur and chlorine compounds [54,59]. At this time we are completing a study (doctoral thesis of Rupert C. C. Perera) of selected atomic and molecular systems in the solid versus the gas state including Ar, CO, CO₂, CCl₄, CHCl₃ and CH₂Cl₂.

C. Development of the Physics and Application of X-Ray Photocathodes

The most successful method applied to date for the measurement of the intensity of the spectra radiated by pulsed high temperature plasma sources (for which the temporal history is also required with as high as picosecond resolution) is based upon the converted signal from the x-ray photocathode as electrons (photoelectrons, Auger electrons and secondary electrons). Most of the electrons ejected from the cathode by the x-ray burst are in the secondary electron region of less than 10 eV--peaking at a few eV or less and with FWHM of less than 5 eV. This is the largest signal component as utilized in the x-ray diode detector and in the high speed x-ray streak and framing cameras [56]. Theoretical models for the yield and for the shape of the secondary electron energy distributions have been derived and found to be in good agreement with our measurements on gold and aluminum for the x-ray photon energy region of 0.1 to 10 keV [57]. Also completed is our companion study on semiconductor and insulator photocathodes. This work has demonstrated the very important fact that certain alkali halides have much higher total quantum yields and with much narrower secondary electron energy distributions than do the usual gold or aluminum photocathodes. We have been able to derive phenomenological models for the prediction of yields and energy distribution curves for the semiconductors and insulators that are in good agreement with our direct measurements [56].

This past year we agreed to participate in a comparative calibration in the low energy x-ray region of two standard x-ray diode detectors of the National Bureau of Standards. (This principal investigator participated in an NBS-sponsored workshop on the evaluation of these inter-lab calibrations held at the Lawrence Livermore Laboratory in June, 1978.)

The current need for precise theoretical and experimental characterization of x-ray photocathodes for high temperature plasma diagnostics is so great that we have been granted by the Department of Energy the support of a post-doctoral research associate to supplement this phase of our AFOSR program. The first appointment was Dr. Jerel A. Smith, a recent doctorate of this physics department. After his work with us he has proceeded on to a California laboratory involved exclusively in plasma diagnostics. Our next appointment has been Dr. John Liesegang from La Trobe University, Australia, who is an internationally recognized specialist in photoemission physics.

We have just completed the design and construction of a new facility for the precise absolute measurement of the total and

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Presented in the following sections are listings of the research publications and of the papers presented at scientific meetings describing the work of this AFOSR program in the grant period 1974-1978. The first-page abstracts of the research publications are presented in Appendix II.

II. RESEARCH PUBLICATIONS OF THIS AFOSR GRANT NO.
75-2762--01 JULY 1974 TO 30 SEPTEMBER 1978
(PUBLISHED, IN-PRESS AND IN PREPARATION)

46. "Low Energy X-Ray and Electron Absorption within Solids (100-1500 eV Region)," Advances in X-Ray Analysis (Plenum Press, New York, 1974) (w/Eric S. Ebsu).
47. "Ultrasoft X-Ray Bragg and Specular Reflection: The Effects of Anomalous Dispersion," Interim Report, AFOSR 72-2174 (August 1974) (w/Rupert C. Perera and Ronald H. Ono).
48. "Demountable Ultrasoft X-Ray Source," (informal notes, August 1974).
49. "Techniques of Low Energy X-Ray Spectroscopy (0.1 to 2 keV Region)," Advances in X-Ray Analysis, (Plenum Press, New York, 1975) (w/Murray A. Tester).
50. "Techniques of Low Energy X-Ray Spectroscopy (0.1 to 2 keV Region)," Interim Report, AFOSR 75-2762 (November 1974) (w/Murray A. Tester).
51. "Valence Band Spectroscopy in the Ultrasoft X-Ray Region (50 to 100 Å), Advances in X-Ray Analysis (Kendall/Hunt, Dubuque, Iowa, 1976), Vol. 19 (w/Kazuo Taniguchi).
52. "Parameters for the Calculation of X-Ray Absorption Coefficients for H (1) through Ge (32) in the 100-1500 eV Region," Advances in X-Ray Analysis (Kendall/Hunt, Dubuque, Iowa, 1976), Vol. 19 (w/Mark L. Schattenburg).

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53. "Quantitative Low Energy X-Ray Spectroscopy (50-100 A Region)," J. Appl. Phys., 47 (1976) (w/Kazuo Taniguchi)
54. "Sulfur LII,III Emission Spectra and Molecular Orbital Studies of Sulfur Compounds," J. Chem. Phys. 64 (1976) (w/Kazuo Taniguchi).
55. "X-Ray Calibration Sources for the 100-1000 eV Region," Proceedings of the 1976 ERDA Symposium on X- and Gamma-Ray Sources and Applications, University of Michigan, Ann Arbor, May 1976.
56. "Secondary Electron Energy Distributions for Gold as Excited by C-K α (277 eV) and Al-K α (1487 eV) X-Rays," Appl. Phys. Lett. 29 (1976) (w/J. A. Smith and D. T. Attwood).
57. "0.1 to 10 keV X-Ray-Induced Electron Emissions from Solids--Models and Secondary Electron Measurements," J. Appl. Phys. 48 (1977) (w/J. A. Smith and D. T. Attwood).
58. "High Efficiency Low-Energy X-Ray Spectroscopy in the 100-500 eV Region," J. Appl. Phys. 49(2) (1978) (w/R. C. C. Perera, E. M. Gullikson and M. L. Schattenburg).
59. "Cl-LII,III Fluorescent X-Ray Spectra Measurement and Analysis for the Molecular Orbital Structure of ClO $\overline{4}$, ClO $\overline{3}$ and ClO $\overline{2}$," J. Chem. Phys. (May 1978) (w/R. C. C. Perera and D. S. Urch).
60. "Some Recent Studies in Low Energy X-Ray Physics," Proceedings of the Eighth International Conference on X-Ray Optics and Microanalysis, Boston, August 1977.
61. "Models and Measurement for the Response of Dielectric X-Ray Photocathodes," Scientific Reports, AFOSR 75-2762-F and DOE E(04-3)235-PA15, March 1978.
62. "Low Energy X-Ray Emission Spectroscopy in the 100-500 eV Region: Molecular Orbital Interpretation," (PhD Thesis by R. C. C. Perera) Special Scientific Report, AFOSR 75-2762-F, May 1978.
63. "The Secondary Electron Emission Photocathode Characteristics for Time Resolved X-Ray Spectroscopy," Proceedings of the International Conference on X-Ray and XUV Spectroscopy, Sendai, Japan, August 1978; Jap. J. Appl. Phys. 17, Suppl. 17-2, p. 129 (1978) (w/ K. Premaratne).

64. "C-K and Cl-L Emission Spectra and Molecular Orbital Analysis of CCl_4 ," Proceedings of the International Conference on X-Ray and XUV Spectroscopy, Sendai, Japan, August 1978; Jap. J. Appl. Phys. 17, Suppl. 17-2, p. 23 (1978) (w/ R. C. C. Perera).
65. "Soft X-Ray Induced Secondary Electron Emission from Semiconductors and Insulators: Models and Measurement," Phys. Rev. B (March 1979 issue) (w/ J. Liesegang and S. D. Smith).
66. "Low Energy X-Ray Emission Spectra and Molecular Orbital Analysis of CH_4 , CCl_4 and CHCl_3 ," J. Chem. Phys. (submitted January 1979) (w/R. C. C. Perera).

Research Papers in Preparation:

67. "Oxygen-K and Carbon-K Emission Spectra and a Molecular Orbital Interpretation for CO and CO_2 ," (w/ R. C. C. Perera).
68. "Total and Differential Secondary Electron Yields for Gold, Copper Iodide and Cesium Iodide in the 0.1 to 10 keV Photon Energy Region," (w/J. Knauer and K. Premaratne).
69. "P-L_{II,III} Fluorescent Spectra Measurements and the Molecular Orbital Analysis for Phosphorous Compounds," (w/F. Fujiwara and B. Young).
70. "Physics and Application of Multilayer 'Crystals' for Spectral Analysis in the 50-100 Å Region."
71. "Parameters for the Calculation of X-Ray Absorption Coefficients in the 0.1 to 20 keV Region," (w/R. G. Hockaday and M. L. Schattenburg).

III. RESEARCH PAPERS PRESENTED AT SCIENTIFIC MEETINGS DURING THE GRANT PERIOD 1974 TO 1978

1974

- Seminar at Lawrence Livermore Laboratory, Livermore, California, August 1974
- Twenty-third Annual Conference on Advances in X-Ray Analysis, Denver, Colorado, August 1974
- Seminar at Los Alamos Scientific Laboratory (University of California), Los Alamos, New Mexico, August 1974
- Seminar at Kirtland Air Force Base and Sandia Corporation, Albuquerque, New Mexico, August 1974

1975

- A two-day symposium on "Low Energy X-Ray and Electron Spectroscopy" held at the University of Hawaii, June 12 and 13. This research group joined others from our chemistry department as host for this meeting which was also part of the Thirteenth Northwest Regional Meeting of the American Chemical Society. Papers presented on this project's research program were:

1. "Some Current Research in Low Energy X-Ray and Electron Physics" (B. L. Henke)
2. "Effect of Chemical State upon Sulfur L_{II}, L_{III} Fluorescence Spectra" (w/ Kazuo Taniguchi)
3. "Effect of Chemical State upon the Characteristic Energy Loss Spectra of Molecular Gases" (w/Taylor Norcross)

(A total of forty-two papers were presented for this symposium from U.S. and international laboratories.)

- Twenty-fourth Annual Conference on Applications of X-Ray Analysis, Denver, Colorado, August 1975
- Seminar at Los Alamos Scientific Laboratory (University of California) Los Alamos, New Mexico, August 1975
- Seminar at Lawrence Livermore Laboratory, Livermore, California, August 1975
- Seminar at Kirtland Air Force Base, Albuquerque, New Mexico, and discussions with E. J. T. Burns, August 1975

1976

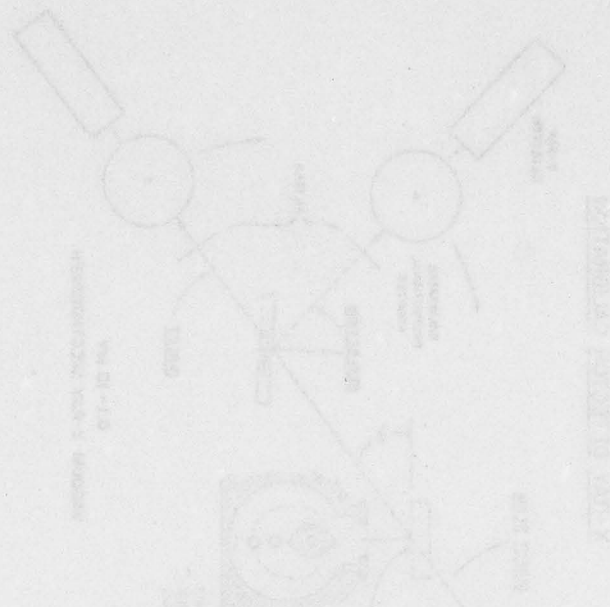
- American Physical Society Topical Conference on Diagnostics of High Temperature Plasmas, Knoxville, Tennessee, January 1976
- ERDA Conference on X- and Gamma-Ray Sources and Applications, University of Michigan, Ann Arbor, Michigan, May 1976
- Seminar at Lawrence Livermore Laboratory, Livermore, California, May 1976

1977

- Seminar at Lawrence Livermore Laboratory, Physics Division, August 1977
- Seminar at Los Alamos Scientific Laboratory, Physics Division, August 1977
- Eighth International Conference on X-Ray Optics and Microanalysis, Boston, Massachusetts, August 1977

1978

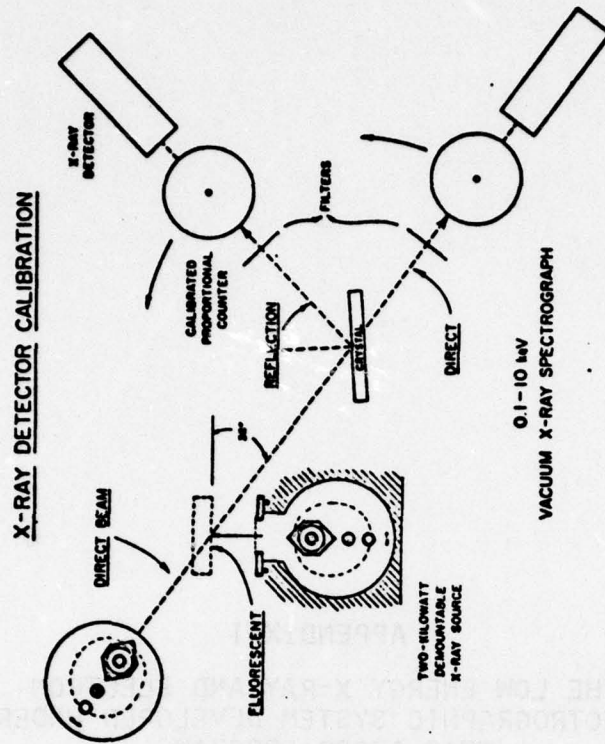
- "A Systematic Study of the Characteristics of X-Ray Photocathodes," Poster Presentation, American Physical Society Second Topical Conference on High Temperature Plasma Diagnostics, Santa Fe, New Mexico, February 28 to March 3, 1978.
- "Application of Low Energy X-Ray Spectroscopic Techniques to High Temperature Plasma Diagnostics," Physics Seminar Lecture, The Los Alamos Scientific Laboratory, June 1978.
- "The Optimization of X-Ray Photocathodes for Time Resolved X-Ray Spectroscopy in Laser-Produced Fusion Research," Physics Colloquium Lecture, University of California Lawrence Livermore Laboratory, June 1978.
- Participated in a workshop on the Absolute Calibration of X-Ray Photocathodes as Applied in X-Ray Detectors (XRD's) sponsored by the National Bureau of Standards at the Lawrence Livermore Laboratory, June 1978. The results of the calibrations of two detectors that were calibrated by each of the six participating laboratories, including this one, were evaluated.
- "The Secondary Electron Emission Photocathode Characteristics for Time Resolved X-Ray Spectroscopy," International Conference on X-Ray and XUV Spectroscopy, Sendai, Japan, August 28 to September 1, 1978.
- "C-K and Cl-L Emission Spectra and Molecular Orbital Analysis of CCl_4 ," International Conference on X-Ray and XUV Spectroscopy, Sendai, Japan, August 28 to September 1, 1978.
- "A Review of X-Ray Photocathode Characteristics that Affect Picosecond Streak Camera Operation," 1978 American Physical Society Annual Meeting of the Division of Plasma Physics, Colorado Springs, October 30 to November 3, 1978.
- Will present a 45-minute invited paper at the American Crystallographic Association Meeting (Joint with Japanese Crystallographic Society), Honolulu, Hawaii, March 26-30, 1979: "Physics and Application of Multilayer 'Crystals' for Spectral Analysis in the 50-100 Å Region."



APPENDIX I

THE LOW ENERGY X-RAY AND ELECTRON SPECTROGRAPHIC SYSTEM DEVELOPED UNDER THIS AFOSR PROGRAM

Figure 1. Ultrasoft X-Ray Vacuum Spectrograph.
 A 2-to-4 kilowatt, demountable x-ray source of characteristic radiation directly, or be used to excite a fluorescent line source of slightly lower photon energy than the exciting line. Langmuir-Blodgett type multilayer analyzers specially developed in this laboratory with 2d-values in the 80-160 Å range are employed for spectral analysis in the 20 to 150 Å region (100-500 eV region). Pulse-height discriminating proportional counter detection is utilized to effectively reduce hard and soft background with better than 60% photon counting efficiency. Appropriate filter-windows in the tenth micron thickness range are used with a vacuum isolation window-gate on the x-ray source and for the proportional counter that is "pressure-tuned" for a given photon energy at subatmospheric pressures, typically 50-to-100 mm of propane counter gas. Spectral data is step-scanned, recorded on paper tape which is then processed on a small laboratory computer. This system is also used for the absolute calibration of x-ray detectors (XRD's) as shown here.



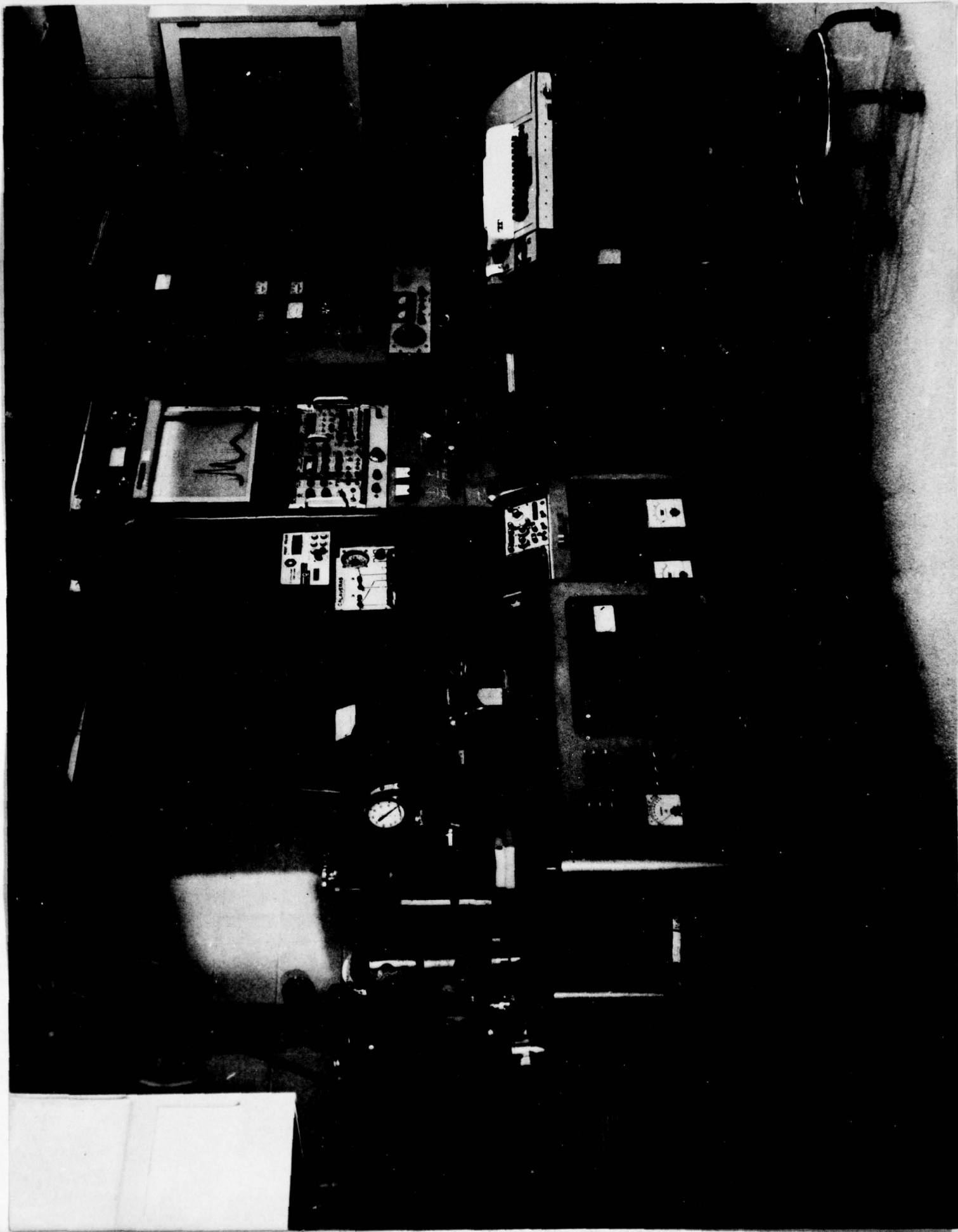


Figure 2. High Resolution, Low-Energy Electron Spectrograph.

A filtered, characteristic line source of low-energy x-radiation is used to excite the photoelectron and subsequent Auger electron and secondary electron spectra from one of eight samples in a rotating holder. The emitted electrons are analyzed with a relative energy resolution of better than 0.3% by a hemispherical lens electrostatic analyzer of mean diameter of 20 inches. The electron counting is with a 16-stage electron multiplier tube. For the measurement of the secondary electron energy distributions of x-ray photocathode materials, the acceptance energy is typically fixed at 15 eV and the accelerating voltage applied to the sample is stepped and the spectra are recorded on paper tape and subsequently processed and plotted with a small laboratory computer system. The measured resolution of the secondary electron energy distributions is better than .05 eV.

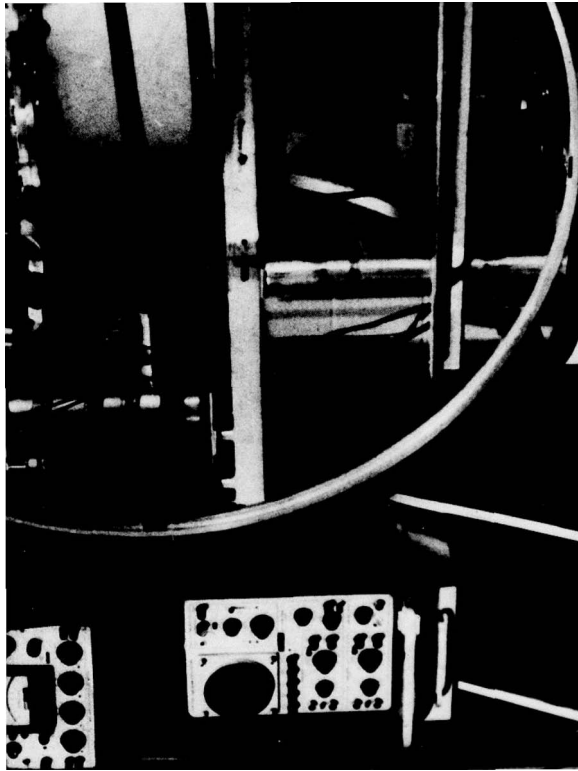
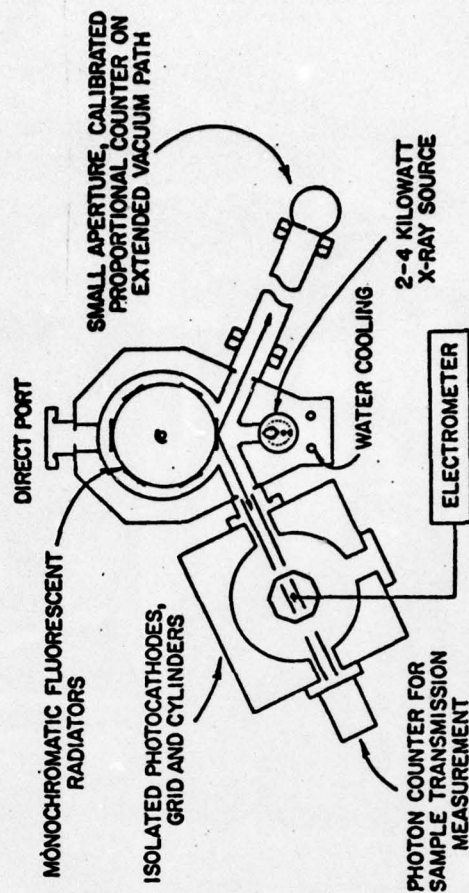


Figure 3. Facility for the Measurement of the Absolute Quantum Efficiency (for Total and Secondary Emission) of X-Ray Photocathode Materials.

A 2-to-4 kilowatt, filtered characteristic line source of x-radiation in the 0.1 to 10 keV region is closely coupled for the excitation of fluorescent line sources of energy just below that of the excitation source. Six fluorescent radiators are mounted on a rotating holder, permitting precise relative measurements. The sample in the radiated position is directly connected to a Carey 401 electrometer system and the photoelectric currents are monitored on an x-ray plotter. Cylindrical electrode systems are used to apply plus-minus 30 volt accelerating potentials to permit a differential measurement for the total and secondary electron yields for either thick or thin (transmission) photocathodes. The photons/steradian flux from the fluorescent source is measured by a calibrated flow proportional counter with the same filter-window as also introduced between the fluorescent source and the photocathode sample. Because of the relatively high photon intensity that is required for precise yield measurements, the absolute photon counter must be on an extended vacuum-pipe path and with an accurately calibrated "pinhole" window. For transmission photocathode studies, a second x-ray detector is used to measure the transmission of the photocathode system to permit a measurement of both the electron yield per incident photon and per transmitted photon.



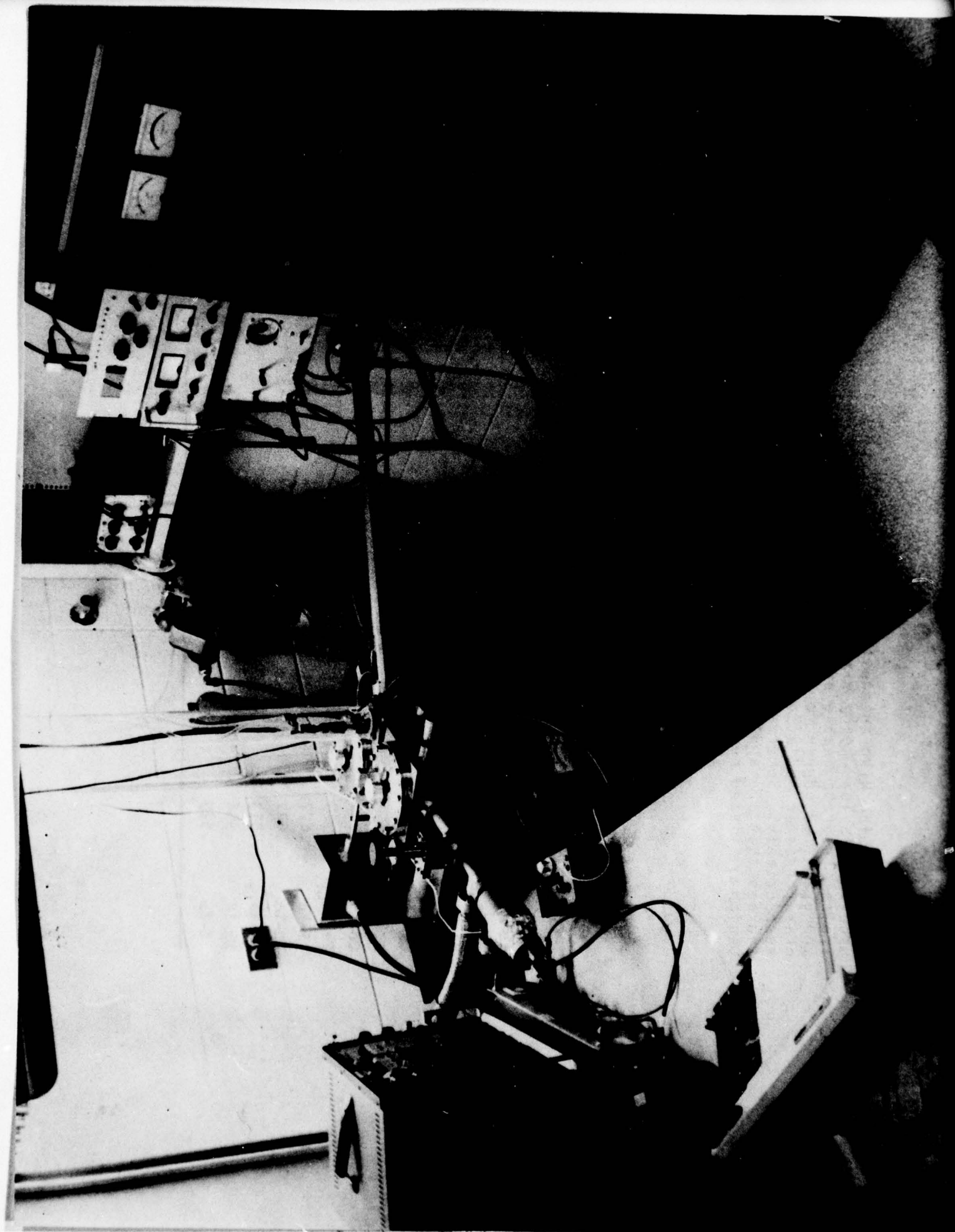


Figure 4. The high intensity excitation source that is used in this low energy x-ray and electron spectroscopy. Typical interchangeable anodes are of copper, aluminum and graphitized copper for the Cu-K, Al-K, Cu-L and C-K characteristic radiations of 8050, 1487, 930 and 277 eV, respectively. Some useful fluorescent radiation line sources that are applied in this work in the low energy region are listed here.

Some Useful Characteristic Line Sources
for Ultrasoft X-Ray Spectroscopy

Line Source	Energy (Kev)	Wavelength (Angstroms)	Line Source	Energy (Kev)	Wavelength (Angstroms)
Al-K $\alpha_{1,2}$	1.487	8.34	Ti-La $\alpha_{1,2}$.452	27.4
Mg-K $\alpha_{1,2}$	1.254	9.89	Ti-L α	.395	31.4
Na-K $\alpha_{1,2}$	1.041	11.9	N-K α	.392	31.6
Zn-La $\alpha_{1,2}$	1.012	12.3	C-K α	.277	44.7
Cu-La $\alpha_{1,2}$.930	13.3	W-N $\alpha_{V,VII}$.212	58.4
Ni-La $\alpha_{1,2}$.852	14.6	Mo-M α	.193	64.4
Co-La $\alpha_{1,2}$.776	16.0	B-K α	.183	67.6
Fe-La $\alpha_{1,2}$.705	17.6	Nb-M α	.172	72.2
F-K α	.677	18.3	Zr-M α	.151	81.9
Mn-La $\alpha_{1,2}$.637	19.4	S-L α	.149	83.4
Cr-La $\alpha_{1,2}$.573	21.6	Y-M α	.133	93.4
Mn-L α	.556	22.3	Sr-M α_1	.114	109.
O-K α	.525	23.6	Be-K α	.109	114.

TWO-KILOWATT ULTRASOFT X-RAY SOURCE

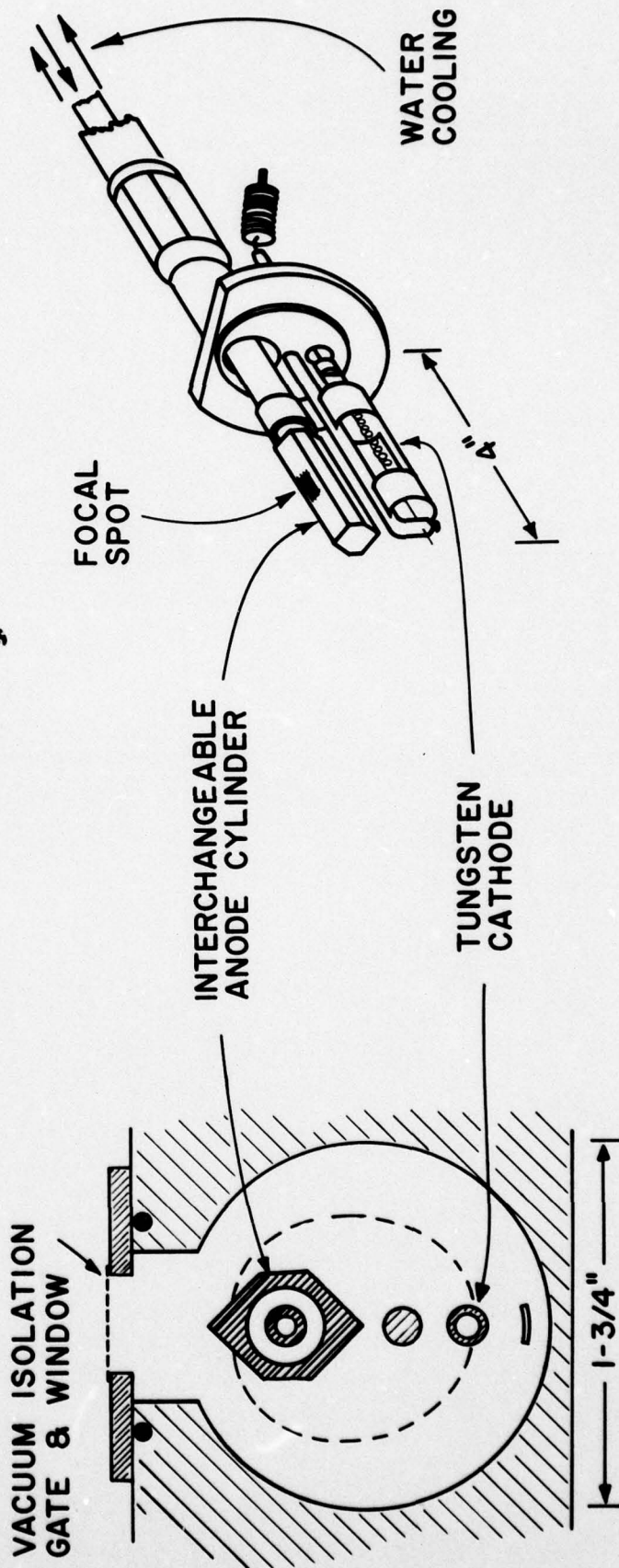
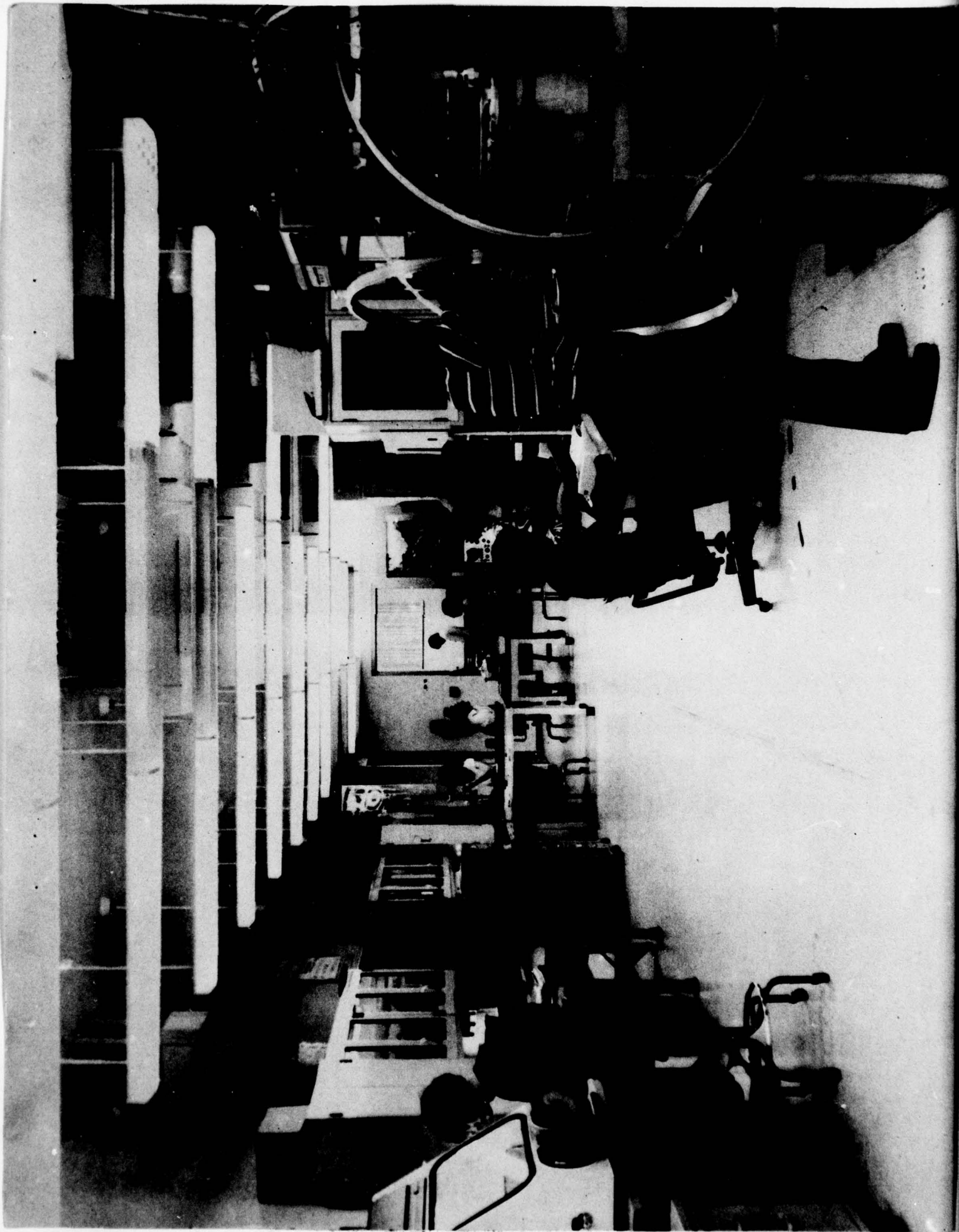


Figure 5. This low energy x-ray and electron spectroscopy laboratory (of more than 2000 square feet). Included are rooms at each end of the laboratory for sample preparation and crystal analyzer construction, and for a small computer and data analysis. Available to this laboratory are such facilities as a large IBM-370 computer system and a large, complete experimental machine shop.



COMPARISON -- THEORY AND EXPERIMENT

LOW ENERGY X-RAY AND ELECTRON ABSORPTION WITHIN SOLIDS
(100-1500 eV Region)

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ABSTRACT

Quantitative analysis by x-ray fluorescence and photoelectron and Auger electron analysis can be effectively extended through a precise knowledge of the total and subshell photoionization cross sections. Light element and intermediate element analysis, as based upon K and L series fluorescence respectively, involve x-ray interactions in the low energy region. Optimized analysis for essentially all the elements by x-ray induced photoelectron and Auger electron spectroscopy involves both x-ray and electron interactions in the low energy region. Unfortunately, theory and measurement for interaction cross sections in this 100-1500 eV region are difficult, particularly for the heavier elements. Nevertheless, recent advances in experimental and computerized-theoretical techniques for the determination of low energy interaction coefficients do permit establishing appreciably more complete tabulations of cross sections than are currently available in this energy region.

In this paper, the types of interaction cross section data that are needed for quantitative x-ray and electron analysis are defined. Such data that are available from experiment and from theory are reviewed and compared. Some newer techniques for the measurement of cross sections are discussed. And finally, new "state of the art" tables are presented for the mass absorption coefficients of all of the elements and of some special laboratory materials. These are tabulated specifically for twenty-six of the most commonly applied characteristic wavelengths in the 8-110 Å region and are based upon the best currently available theoretical and experimental data.

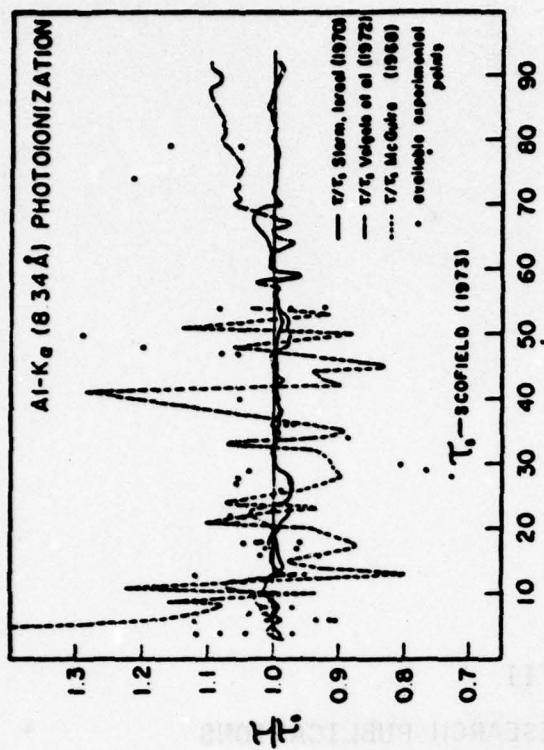


Figure 1

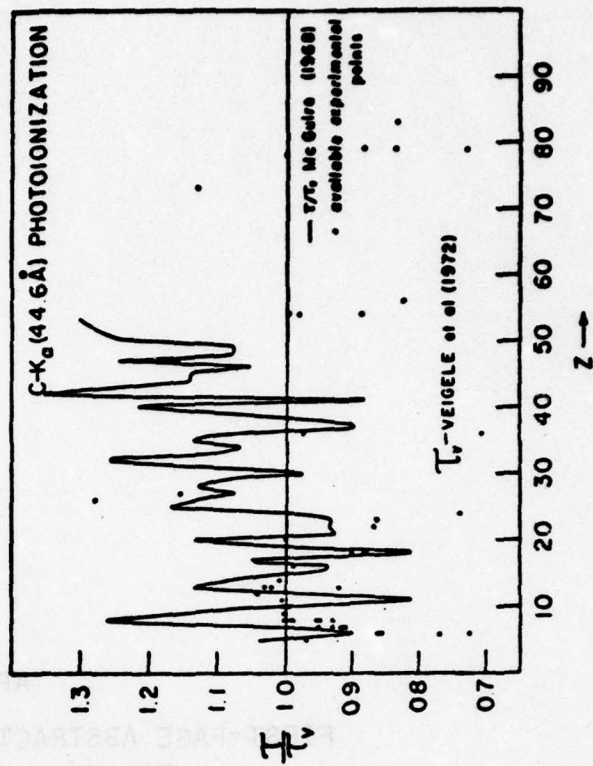


Figure 2

ULTRASOFT X-RAY BRAGG AND SPECULAR REFLECTION: THE
EFFECTS OF ANOMALOUS DISPERSION

B. L. Henke, R. C. C. Perera and R. H. Ono

ABSTRACT

For the low energy x-rays (100-1000 eV region), atomic scattering becomes of practical importance as it is involved in Bragg reflection from crystal analyzers and in specular reflection from mirror systems. But the cross section for coherent scattering in this energy region is very small as compared with that for photoionization, the latter being more amenable to direct measurement and also to theoretical calculation. Assuming dipole descriptions only need to be considered here where the wavelengths are long as compared with orbital dimensions, the current theoretical partial photoionization cross section calculations have been applied to yield oscillator densities which permit a numerical solution of semi-classical dispersion integrals to obtain the atomic scattering factors. These factors account for the strong anomalous dispersion that is characteristic of low energy x-ray scattering. For the long x-ray wavelengths, it is assumed that all atomic electrons scatter from a volume that is small as compared with the wavelength, in phase in all directions. The atomic scattering factors, in turn, are applied with electromagnetic theory to calculate optical constants for the solid and structure factors that characterize the crystalline state. With these, the classic models for x-ray reflection as the Darwin-Prins perfect crystal theory and the mosaic, imperfect crystal theory, have been specialized for the low energy x-ray region and applied to calculate the reflection properties of specific, practical analyzers for the ultrasoft x-ray wavelengths as the acid phthalate crystals and the Langmuir-Blodgett multilayers with d-spacings in the 25 to 150 Å range. And with the optical constants, the Fresnel equations have been expressed for the long x-ray wavelengths and for the large angle region to calculate the specular reflectivities for the fused quartz and the aluminum mirror systems. These theoretical Bragg and specular reflection characteristics have been compared to those as measured for the same systems and generally good agreement has been found between theory and experiment. Finally, this approach for the calculation of anomalous dispersion effects has yielded a relatively simplified description of the general properties of dispersive analyzers for the low energy x-ray region.

TECHNIQUES OF LOW ENERGY X-RAY SPECTROSCOPY

(0.1 TO 2 keV REGION)

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ABSTRACT

Presented here is a report on the development of practical techniques for laboratory spectroscopy in the 5 to 150 Å wavelength region as may be applied, for example, to light element and surface state analysis, high temperature plasma diagnostics and to the design and calibration of x-ray astronomy measurements.

I. INTRODUCTION

X-ray spectroscopy in the low energy region at or below one kilovolt has become of considerable practical importance for light element analysis, valence band or orbital energy analysis, surface characterization and high temperature plasma diagnostics. The light elements, Mg through Be, emit characteristic x-radiation only in this region. The sensitive transitions from the outer orbitals into the first inner shells yield valence band spectra which are always in the ultrasoft wavelength region. Fluorescence analysis based upon the ultrasoft K, L or M characteristic wavelengths typically involve sampling depths of surfaces in the sub-micron range. And, finally, the spectra emitted by high temperature plasmas in the one-to-ten million degree range emit most strongly in this low energy region and do characterize the plasma temperature and electron-ion densities--such plasmas are involved in controlling nuclear reaction research and are of particular importance in laser-induced x-ray sources, and are also often observed from astronomical sources via rocket and satellite studies.

Advances in X-Ray Analysis (Kendall/Hunt,
Dubuque, 1976) Vol. 19, pp. 627-641

VALENCE BAND SPECTROSCOPY IN THE ULTRASOFT X-RAY REGION (50 TO 100 Å)

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ABSTRACT

Transitions from the valence electron levels into the first relatively sharp inner sub-shell levels result in characteristic x-ray emissions in the 100-200 eV region. These spectra sensitively reflect the chemical state of the atoms which are representative of the sub-micron thickness of the sample surface under low energy x-ray excitation and of the first few molecular layers of the sample under electron excitation.

An optimized measurement method for this 50-100 Å spectral region is based upon single crystal spectrometry using a lead stearate analyzer which has high dispersion and efficiency and an energy width of about one eV in this wavelength range. Spectra are recorded using "tuned" proportional counter detection. In the work reported here, low energy x-ray excitation is used in order to minimize the possibility of radiation damage of the sample.

Each spectrum is calibrated for both energy and instrument transmission using known, sharp M lines of elements such as molybdenum, zirconium and yttrium which will bracket the spectral range under measurement. A simple method has been developed for "stripping" from the measured spectra the Lorentzian crystal width and the Gaussian collimation width in order to allow an estimation to be made of the actual emission line widths as well as the relative intensities.

In this report, as an illustrative application example, S-LII,III spectra are presented for a series of sulfur compounds in both solid and gas states. Manne's approximate molecular orbital interpretation of the x-ray emission spectra has been adopted and extended to apply to the LII,III spectra for second row elements.

Advances in X-Ray Analysis (Kendall/Hunt,
Dubuque, 1976) Vol. 19, pp. 749-767

APPENDIX

PARAMETERS FOR THE CALCULATION OF X-RAY ABSORPTION COEFFICIENTS
FOR H (1) THROUGH Ge (32) IN THE 100-1500 eV REGION*

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In a recent paper¹ we compiled absorption coefficient tables for all elements through atomic number 94 (and for some often used laboratory compounds) for twenty-six K, L, and M characteristic wavelengths as commonly involved in low energy x-ray spectroscopy in the 8.34 to 114 Å region. These tables were based upon a "state-of-the-art averaging" of available experimental data and the theoretical data of Veigele, *et. al.*² and of Scofield³. Our best experimental data (on the inert gases) were fit closely by the theoretical photoionization cross section curves (except for Xenon at the longer wavelengths) thereby verifying that for this low energy region coherent and incoherent scattering contributions to x-ray absorption are essentially negligible and that only small adjustments in the theoretical data were appropriate at this time.

In order to facilitate the programming of absorption corrections in quantitative, low energy x-ray analysis, we have listed here the parameters which define a least squares fit to all of the absorption data for the first thirty-two elements (through Germanium) using polynomials of the form

$$\log (10^{-1}\mu) = a + b \log E + c (\log E)^2 + d (\log E)^3$$

(μ in cm²/gm, E in eV and log terms to base ten.)

These polynomials were used to plot the associated absorption curves within the listed absorption edge energies. In order to compare these curves to available experimental data the measured values have also been plotted (solid dots indicate our measurements and crosses indicate most other reported measurements). The sources of the experimental data are listed in Reference 1.

Using these parameters, we have programmed a small laboratory computer to generate tables and plots for compound absorbers. Included here are the calculated absorption curves for the molecules C₂H₆, C₂F₆, H₂S, and CCl₄ along with our directly measured absorption cross sections for these compounds in order to illustrate the additivity of atomic cross sections for this low energy region.

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²W. J. Veigele, *Atomic Data Tables* 5, 51 (1973).

³J. H. Scofield, Technical Report No. 51326 (1973), University of California Radiation Laboratory.

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Quantitative low-energy x-ray spectroscopy (50–100-Å region)*

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The quantitative analysis of emission spectra in the 10–100-Å region has become of considerable importance for high-temperature plasma diagnostics (10^6 – 10^7 °K region) and for molecular orbital and solid-state-band analysis. Because measurement intensities are typically low in these applications, achieving an optimum spectrographic measurement is essential. In order to present specific procedures and methods for optimizing and calibrating a low-energy spectrographic measurement, a molecular orbital analysis in the 70–90-Å region ($S-L_{II,III}$ emission spectra) has been carried out quantitatively in energy and intensity using a recently described single-crystal (lead stearate) spectrographic approach with about 1 eV resolution. Radiative yields, Y , for the radiation process being investigated are determined by the relation, $Y = Z/(X_0 RSTQ)$, where Z is the area (intensity \times angle) under the spectrographic line, X_0 the excitation function, $R(\lambda)$ the coefficient of reflection of the analyzer, $S(\lambda)$ the effective source thickness, $T(\lambda)$ the window transmission, and $Q(\lambda)$ the quantum counting efficiency of the detector. The determination of each of these parameters has been considered in detail.

PACS numbers: 32.10.F, 32.10.Q, 52.70., 07.85.

I. INTRODUCTION

Low-energy x-ray spectroscopy in the 10–100-Å wavelength region (100–1000-eV energy region) has become of considerable interest as applied in two types of research:

(1) High-temperature plasma analysis. Ionized gases (plasmas) in the 10^6 – 10^7 °K temperature range radiate strongly in the 100–1000-eV x-ray region (1 eV corresponds to about 10^4 °K). Because such high-temperature plasmas are characteristic of important astrophysical sources, their analysis is a fundamental aspect of the relatively new science of x-ray astronomy. And now it has become possible to generate such plasmas in the laboratory which radiate sufficiently strongly in the x-ray region for spectroscopic analysis. These are developed magnetohydrodynamically and magnetically confined, or by pulsed laser or electron beams and inertially confined. An important application of such high-temperature plasma analysis is for controlled thermonuclear fusion research. The x-ray measurements can yield information as to the temperature, density, time history, and spatial characteristics of the plasma.¹

(2) Molecular orbital and solid-state-band analysis. When an atom is singly ionized with a vacancy created in one of its higher inner core levels, this vacancy is then promoted to one of the outermost electronic levels and a radiative transition typically in the 100–1000-eV region may result. The electronic structure of the initial ionization state of the atom is relatively insensitive to its molecular or condensed matter environment, but that of the final ionized state is strongly affected by this atomic environment. The major features of the associated x-ray emission spectra can yield direct information as to the populations, energy levels, and widths (or band structure) of the outer electronic levels. Because the strong radiative transitions obey the dipole selection rules, information as to the symmetry character of the outer electronic states may also be gained. Finally, the degree of localization of certain outer levels relative to a particular ionized atom can

often be revealed by the existence of molecular orbitals rather than band structure and by comparative analyses of such spectra originating from inner-core vacancies on adjacent atoms. Such low-energy x-ray emission spectra can be directly applied, using standard sample systems, for the identification of unknown valence states. These spectra can be applied to establish and to test molecular orbital and/or band theory models for which computer analysis is rapidly becoming more practical and precise.^{2,3}

Typically, low-energy x-ray emission spectra of interest are of low intensities. At these transition energies, radiative transition rates are small as compared with those for the competing Auger and Coster-Kronig processes. For this reason it is generally required that the low-energy spectroscopy be by methods of optimum efficiency. Usually, the characteristically low emission intensities will not permit the use of double crystal spectrometry or of high-resolution grating spectrographs. The basic spectrographic approach that is used in this laboratory is shown in Fig. 1. It is

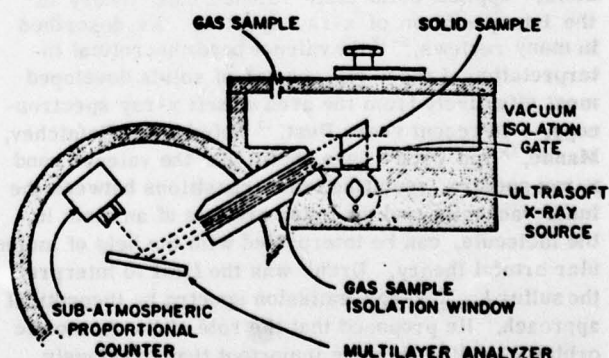


FIG. 1. A single-crystal spectrographic approach for low-energy x-ray spectroscopy applying closely coupled 2-kW demountable x-ray source, large d -spacing crystal analyzer, and tuned subatmospheric pressure proportional counter.

Sulfur $L_{II,III}$ emission spectra and molecular orbital studies of sulfur compounds

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The fluorescent sulfur $L_{II,III}$ emission spectra have been quantitatively measured and analyzed for the relative strengths (radiative yields) of the allowed transitions, and for the corresponding emission linewidths. These were investigated for the sulfur compounds in the solid, vapor, and gas states— Na_2SO_4 , K_2SO_4 , CdSO_4 , Na_2SO_3 , K_2SO_3 , $\text{C}_2\text{H}_5\text{S}$, H_2S , SO_2 , and SF_6 . The S $L_{II,III}$ spectra for the solid compounds (all strongly ionic) revealed essentially the same localized molecular orbital character about a central sulfur atom as for the molecular compounds—showing no significant influence of the cations and no evidence of crystal band structure. The measured molecular orbital energies and radiative yields were found to be generally consistent with the eigenvalue and eigenvector calculations based upon current CNDO and *ab initio* molecular orbital approximation methods. The measured sulfur $L_{II,III}$ spectra for the compounds reported in this paper have been interpreted according to the valence orbital configuration as obtained from the CNDO/2 method. This is done while recognizing that other reported molecular orbital calculations on these molecules often indicate different orderings. The molecular orbital energies as derived from the $L_{II,III}$ spectra have also been compared with those obtained from photoelectron spectroscopy, demonstrating, generally, very good agreement between these two methods. Because the $L_{II,III}$ spectra for second row elements probe the 3s and the 3d character of the valence band and the K_α spectra probe the 3p character of the valence band, it has been found very useful to combine the results of these x-ray emission techniques in order to gain a complete analysis of valence band electronic populations and symmetries. It has been shown that the $L_{II,III}$ emission analysis can be a uniquely powerful tool for the determination of the role of the 3d atomic orbital in the chemical bonding of the second-row elements.

I. INTRODUCTION

X-ray spectroscopy has long been a basic method for studying the elemental compositions of materials and the electronic structure of atoms. Siegbahn,¹ in the early 1900's, developed the technique for measuring x-ray emission and absorption spectra of many elements. It has been known since 1920 that the x-ray spectrum of an element varies according to its state of chemical combination. Lindh² noted the chemical effect upon the K-absorption spectra for sulfur compounds. Later, Lindh and Lundquist³ were able to observe the chemical combination effect in x-ray emission spectra.

Skinner and O'Bryan^{4,5} showed the importance of x-ray spectroscopy in their investigations of valence electron band structure. Sommerfeld and Bethe,⁶ and later Seltz,⁷ applied solid state valence band theory to the interpretation of x-ray spectra. As described in many reviews,⁸⁻¹² the valence band theoretical interpretation of the x-ray spectra of solids developed most effectively from the area of soft x-ray spectroscopy. In recent years Best,¹³ Nefedov and Fomichev,¹⁴ Manne,¹⁵ and Urch¹⁶ have shown that the valence band x-ray spectra, resulting from transitions between the inner vacancies and the outer orbitals of an atom in the molecule, can be interpreted with the help of molecular orbital theory. Urch¹⁷ was the first to interpret the sulfur $L_{II,III}$ x-ray emission spectra by theoretical approach. He proposed that the role of the 3d atomic orbital of sulfur is more important than previously speculated. Manne¹⁵ interpreted the x-ray emission spectra of gaseous molecules by molecular orbital theory. He proposed that the relative intensities of x-ray transitions from the molecular orbitals were related to the eigenvectors of an LCAO (linear combination of atomic or-

bitals) molecular orbital. This same relation has been used for some solid compounds¹⁷⁻²⁵ and satisfactory results have been obtained. Many investigators¹²⁻²⁵ have shown that molecular orbital theory could be used effectively for the interpretation of the effect of chemical bonding upon the valence electron x-ray emission spectrum.

Today the valence molecular orbital structure is fairly well understood, particularly from the theoretical point of view. Most of the experimental results have been obtained from the K_α emission spectra (see, for example, Refs. 18-27). For the second row elements, K_α emission spectra result from transitions from the valence orbital levels to the 1s level, thereby revealing only the 3p character in the valence band spectra. $L_{II,III}$ emission spectra result from transitions from valence orbital levels to the 2p level for the second row elements, and, therefore, by measuring these spectra, we can investigate the 3s and 3d character in the valence band. By analyzing the $L_{II,III}$ emission spectra along with the K_α emission spectra and/or the photoelectron spectra, a more comprehensive view of the molecular orbital structure in the valence band can be gained.

The sulfur $L_{II,III}$ emission spectra for solids have been previously obtained by Henke²⁸ and by Merritt and Agazzi²⁹ through the secondary excitation method, and by Meisel *et al.*³⁰ and Nefedov and Fomichev¹⁴ through electron excitation. Very recently Sadovskii *et al.*³¹ measured the sulfur $L_{II,III}$ fluorescence spectra for gaseous compounds and interpreted these with the help of molecular orbital theory. Most reported measurements and interpretations of $L_{II,III}$ emission spectra to date have been incomplete and inexplicit, however. In recent years, the photoelectron spectra from molec-

X-RAY CALIBRATION SOURCES FOR THE 100-1000 eV REGION*

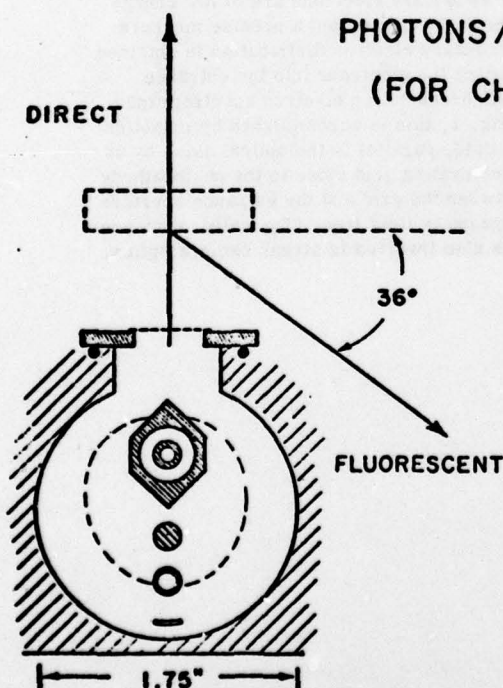
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In order to calibrate windows, detectors and dispersive analyzers for low energy x-ray spectroscopy, certain characteristic line sources have been found to be particularly useful. These are obtained directly from an appropriate anode of a two-kilowatt demountable x-ray source, or from a fluorescent secondary radiator that is coupled closely to the x-ray source as shown in Fig. 1. Often the characteristic lines may be effectively isolated by filter and/or by pulse height discrimination with a proportional counter.¹ This is possible in the low energy x-ray region because the spectral line series are simpler and the line intensity relative to the associated continuum background is considerably higher than that for the ordinary x-ray region. This is illustrated in the spectra presented

in Figs. 2 through 13 of fluorescent line sources in the 100 to 1000 eV region (10 to 100 Å region). Also presented are typical absolute intensities as measured off a crystal analyzer and directly from the fluorescent radiator. The absolute characteristic radiation output intensities from three often-used anode sources for the excitation of the fluorescent lines are listed in Fig. 1. All intensities were measured with a calibrated proportional counter and with the window set to accept the full pulse height distribution. The measured intensities were divided by the appropriate x-ray tube window transmission. (Typical window transmissions are 50 to 80%.) The demountable x-ray source that is used in this laboratory is described in Fig. 14.

DIRECT SOURCE INTENSITY - I
PHOTONS/SEC - STEARADIAN-KILOWATT
(FOR CHARACTERISTIC RADIATION)



ANODE	RADIATION	I
ALUMINUM	Al-K _α (8.34 Å / 1490 eV)	6 x 10 ¹³
COPPER	Cu-L _α (13.3 Å / 930 eV)	6 x 10 ¹³
GRAPHITED COPPER	C-K _α (44.7 Å / 277 eV)	2 x 10 ¹⁴

Fig. 1. Showing the direct and fluorescent x-ray source geometries. Also listed are typical, absolute characteristic radiation output intensities from aluminum, copper and graphited anodes as used in the excitation of the fluorescent spectra shown in Figs. 2 through 13.

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Secondary electron energy distributions for gold as excited by C K_{α} (277 eV) and Al K_{α} (1487 eV) x rays

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The secondary electron energy distributions for a gold photocathode as excited by C K_{α} (277 eV) and Al K_{α} (1487 eV) x rays have been measured. The shapes of the energy distributions are essentially the same for these two x-ray photon excitation energies. For thick evaporated gold samples on glass substrates (at 150°C and 3×10^{-4} Torr), the secondary electron energy distributions peak at about 1 eV and have a FWHM of about 4 eV. As measured immediately after ion cleaning, the distributions peak at about 2 eV and have a FWHM of about 6.6 eV. Approximately 5 h after ion cleaning, the measured distributions appear as those obtained before ion cleaning. The work function of the evaporated gold photocathode temporarily increases by 1 eV upon ion cleaning.

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The photoelectric conversion of x-ray intensity into secondary electrons¹ has become of considerable interest and importance in the development of detectors and of streak²⁻³ and framing⁴ cameras for application to the diagnostics of high-temperature plasma sources of intense x radiation. The photocathode response as a function of the incident x-ray photon energy is required for quantitative measurement. The energy spread (the secondary electron energy distribution) must be known in order to evaluate the time resolution of the picosecond streak cameras now under development.

There have been no precise measurements of x-ray-induced secondary electron distributions reported to this time. The mechanisms for the internal excitation, transport, and escape of the secondary electrons are not well known. Considerably more experimental data must be obtained before an adequate theory for the x-ray generation of secondary electrons can be presented. We have initiated a program of measurement of the second-

ary electron distributions for practical photocathode materials as excited by calibrated monoenergetic x-ray line sources^{5,6} in the 100–10 000-eV region. A report is now in preparation⁷ that describes the models and methods which we have chosen for these measurements along with our first measurements on the gold photocathode. In this letter, we present an outline of our measurement procedure and some of these first results.

Because the secondary electrons are of low energy (typically in the 0–30-eV region) a precise measurement of the secondary electron distribution is obtained by preaccelerating the electrons into the entrance aperture of a high-resolution electron spectrograph. As shown in Fig. 1, this is accomplished by establishing a uniform field, parallel to the optical axis, by using a plane accelerating grid close to the photocathode. The region between the grid and the entrance aperture of the spectrograph is field free. (Typically, such preacceleration is also involved in streak camera optics,

0.1-10-keV x-ray-induced electron emissions from solids—Models and secondary electron measurements

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Analytical models are presented describing the x-ray-excited emission of "no-loss" photoelectrons and Auger electrons and the energy distribution of emitted secondary electrons. The secondary electron energy distribution is given in terms of the electron kinetic energy E_K , work function W , photon energy E_γ , and mass photoionization coefficient $\mu(E_\gamma)$, as proportional to $E_K \mu(E_\gamma) E_K (E_K + W)^{-4}$. Techniques of electron spectral measurements utilizing uniform field preacceleration and limited acceptance angle spectrometers are discussed. Secondary electron energy distributions are measured at about 10^{-8} Torr from thick evaporated films of gold and aluminum at photon energies 277, 1487, and 8050 eV. The shapes of these distributions do not depend significantly upon photon energy. The full width at half-maximum (FWHM) of these distributions are 3.9, 6.7, and 4.4 eV for Au and ion-cleaned Au and Al photocathodes, respectively. The data agree well with the model predictions.

PACS numbers: 79.60.Cn, 73.30.+y, 72.10.Bg

I. INTRODUCTION

This work is in sequel to and in support of a recent presentation by the authors of some measurements on the secondary electron energy distributions from gold as excited by C-K α (277 eV) and Al-K α (1487 eV) x-ray photons.¹ It is an attempt to present the basic physics for the measurement and for the interpretation of the x-ray-induced electron emissions from uniform isotropic solids.

In Fig. 1 are shown the typical characteristics of an electron spectrum induced by an x-ray beam incident upon a solid. Illustrated here are the sharp photoelectron and Auger electron "no-loss" lines with their characteristic energy loss tail structure, along with the low-energy secondary electron distribution. In contrast to uv-excited electron spectra, here the photoelectrons and the principal sharp Auger electron emissions are well outside the low-energy secondary electron energy region. The secondary electron spectrum peaks at about 1 to 2 eV and has a full width at half-maximum (FWHM) that is usually below 10 eV. In this 0-30 eV interval are typically from 50 to 90% of the total number of electrons emitted for photon excitation in the 100-10000-eV region.

The x-ray-excited electron spectra constitute a unique "window" into the solid and its electron excitation, transport, and escape processes. When a thorough understanding of the physics of these processes is gained, electron spectroscopy can provide an important quantitative basis for the physical and chemical analysis of solids. The electron spectroscopy for chemical analysis (referred to as ESCA or XPS) has become a well-recognized research area within the last ten years.²

The photoelectric conversion of x-ray intensity into electron emission can provide an important practical basis for x-ray intensity measurement. X-ray photoelectric detectors are vacuum devices and, unlike gas ionization detectors, can be windowless. A unique advantage of the photoelectric detector is that it can be

applied effectively over a wide band of photon energies.^{3,4}

A very recent application of secondary electron detectors has been in the development of streak and framing cameras for the diagnostics of x-ray bursts from laser-produced plasmas. The time spread in the photoconverted secondary electron emission per photon is probably of the order of 10^{-14} sec, and the energy spread is of the order of 10 eV. An x-ray source can be imaged and photoconverted to an electron source which may then be reimaged down a streak or framing camera tube with an accelerating electron lens system. The time history of an x-ray event can be obtained by a fast transverse deflection of this image, e.g., to form a "streak" pattern with a time resolution in the picosecond range.^{1,5-9}

In order to support research and application in x-ray photoemission, considerably more theoretical and experimental work should be done on the development of a quantitative relationship between the electron emission spectrum, the incident photon energy, and the characteristics of the photocathode. There is no complete theory of x-ray photoemission that is available

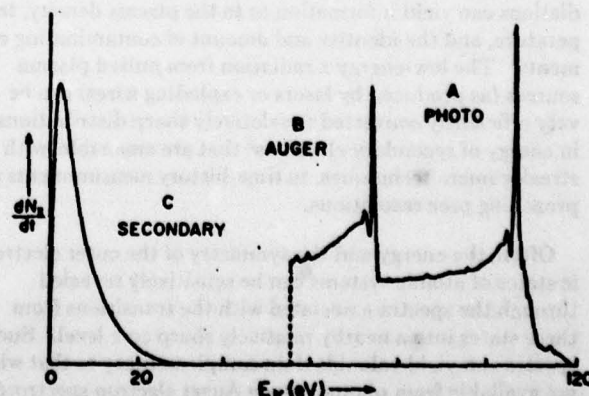


FIG. 1. A typical x-ray-excited photoemission spectrum.

High-efficiency low-energy x-ray spectroscopy in the 100–500-eV region

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The lead myristate multilayer analyzer has provided a basis for a relatively simple and efficient spectroscopy for the low-energy x-ray emissions in the 20–80-Å region (where conventional crystal spectroscopy and grazing incidence grating spectroscopy are generally inefficient). The percent reflectivity, the integrated coefficient of reflection, and the Bragg diffraction width of the lead myristate analyzer have been measured and found to be consistent with the predictions of a simple theoretical model for multilayer diffraction. This multilayer spectroscopy at large Bragg angles has a high efficiency (high instrument transmission) as compared to grazing incidence grating spectroscopy in this 20–80-Å region. However, the resolution is limited to that set by the diffraction width of the lead myristate analyzer of about 1 eV. Because the collimator-crystal broadening function can be precisely defined, a simple and effective deconvolution procedure can be applied with this multilayer spectroscopy to bring the resolution into the sub-electron-volt region. To demonstrate the efficiency of lead myristate spectroscopy in the 20–80-Å region, spectra were measured and analyzed from x-ray excited fluorescent sources which are characteristically of low intensity. (X-ray excitation yields a minimum of background spectra and of radiation damage.) These include the $L_{2,3}$ atomic spectrum of argon and the C-K molecular spectrum of CO_2 , both in the gas phase, and the Cl- $L_{2,3}$ and O-K spectra from solid lithium perchlorate. Many samples undergo appreciable radiation-induced chemical change during the exposure time that is required for measurement—even with an optimally fast spectrograph and with fluorescent excitation. A method has been developed to evaluate and to correct for radiation damage by distributing the exposure over an effectively large sample volume either by gas flow or by rotating through multiple samples during measurement. Several spectral scans were made on the LiClO_4 using six samples. The total exposure time for each data point in each scan was recorded which permitted an extrapolation into a “zero” exposure spectrum. Finally, Fe- $L_{2,3}$ /O-K spectrum (from Fe_2O_3) in the 17–25-Å region is presented to illustrate the effectiveness of the lead myristate analyzer in third-order diffraction. For this multilayer, the third-order diffraction efficiency is one-third that of the first order and is nearly twice that of the second order for this wavelength region.

PACS numbers: 07.85.+n, 32.30.Rj, 52.70.Kz, 33.20.Rm

I. INTRODUCTION

There are two areas in which low-energy x-ray spectroscopy is of particular importance at this time—the diagnostics of high-temperature plasmas¹ and the determination of the chemical and solid-state electronic structure of atomic systems.²

In the controlled thermonuclear fusion research, a critical temperature region of current interest is in the $(1-10) \times 10^6$ °C range. The plasmas involved emit radiations most characteristically in the low-energy x-ray region (100–1000 eV/10–100 Å). The detailed spectroscopy of these plasma radiations can yield information as to the plasma density, temperature, and the identity and amount of contaminating elements. The low-energy x radiation from pulsed plasma sources (as produced by lasers or exploding wires) can be very efficiently converted to relatively sharp distributions in energy of secondary electrons³ that are amenable, with streak camera techniques, to time-history measurements approaching psec resolutions.

Often, the energy and the symmetry of the outer electronic states of atomic systems can be sensitively revealed through the spectra associated with the transitions from these states into a nearby relatively sharp core level. Such spectra can yield valuable data complementary to that which are available from photoelectron Auger electron spectroscopy on the structure of valence bands, solid-state bands, and molecular orbitals.⁴ These sensitive first transitions into

the core levels typically result in low-energy x-ray spectra at a few hundred eV or less.

Using, for example, the acid phthalate crystals (2d value of about 26.6 Å), the conventional x-ray crystal spectroscopy has been very effectively extended down to about 500 eV.⁵ Extreme ultraviolet diffraction grating spectroscopy has been extended with high efficiency (with relatively large angles of grazing incidence) up to about 100 eV.⁶ We have found that a very efficient spectroscopy in the gap region of 100–500 eV is by using the multilayer analyzers as the lead stearate and lead myristate of 2d values equal to 100 and 80 Å, respectively. We have recently presented the detailed characteristics and application of the lead stearate analyzer.^{7,8} In this paper, we extend the presentation of the methods and techniques of low-energy x-ray spectroscopy as specially applied with the lead myristate analyzer.

In Secs. II–V, we present an analysis and measurements of the x-ray optical characteristics of this multilayer analyzer, an optimized spectroscopic and data analysis procedure for gaining maximum overall efficiency and resolution, and, finally, we present some examples of applications to atomic and molecular low-energy x-ray spectroscopy.

II. REFLECTION PARAMETERS FOR THE LEAD MYRISTATE MULTILAYER

Lead salts of the fatty acids deposited as Langmuir-Blodgett multilayers have been demonstrated to be highly efficient

Cl- $L_{II,III}$ fluorescent x-ray spectra measurement and analysis for the molecular orbital structure of ClO_4^- , ClO_3^- , and ClO_2^-

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The chlorine $L_{II,III}$ low energy x-ray spectra from sodium perchlorate, chlorate and chlorite have been obtained using carbon K_α (277 eV) photon excitation and a lead myristate analyzing "crystal" ($2d = 80$ Å). X-ray induced decomposition was observed for each of these compounds. By taking repeated spectral scans, systematically distributed over six samples, it was possible to extrapolate to "zero-dose" Cl- $L_{II,III}$ spectra. A specially developed least-squares fitting program was applied to precisely determine the energy and strength of each spectral component which utilized the known collimation and crystal broadening functions and yielded energy resolutions of less than 1 eV. Broad low-energy satellite structures were observed for all the oxy-anions and for chloride (NaCl) and have been compared to similar satellites as measured in the Ar- $L_{II,III}$ spectrum. These structures were thus identified as resulting from multielectron processes. The other peaks in the Cl- $L_{II,III}$ spectra of the oxy-anions could be understood as corresponding to transitions from molecular orbitals with Cl 3s or 3d character. These results have demonstrated that 3d orbitals do play a definite role in the formation of chemical bonds in the oxy-anions of chlorine and that the importance of this role increases with the oxidation state of the chlorine. Satisfactory correlations have been obtained with the complementary K_α x-ray emission and photoelectron spectra and with molecular orbital theory for the same anions.

I. INTRODUCTION

Transitions between the molecular orbital states and the nearby and relatively sharp core level states result in low energy x-ray spectra that typically lie in the 100–300 eV (40–100 Å) region. Such spectra can sensitively portray the orbital structure of the molecule (or, in many cases, of an ionic group). For the second-row elements, the nearest core levels are the $2p_{1/2}$ – $2p_{3/2}$ spin-orbit split states. The atomic binding energies of these $L_{II,III}$ levels, for example, for 15 P, 16 S, 17 Cl, and 18 Ar are 136–135, 165–164, 202–200, and 247–245 electron volts, respectively. In a particular chemical environment, these core levels of a given atom may shift as much as 10 eV. Such core level chemical shifts can be measured by x-ray photoelectron spectroscopy (XPS). The molecular orbital energies are of the order of 10 eV and can also be measured directly by ultraviolet photoelectron spectroscopy (UPS). The x-ray emission spectra directly yield the difference in the energy of the molecular orbitals and the core level states. However, unlike the photoelectron spectra, the x-ray emission spectra reveal appreciable information about the symmetries of the molecular orbital states. The $L_{II,III}$ spectral intensities are determined mostly by the *s* and *d* character of the orbitals and the K_α spectral intensities are determined mostly by the *p* character of the orbitals. If the $L_{II,III}$ or K_α spectrum originates from an atom of a molecule or of a strongly ionic group that contains only one such atom, it is then relatively easy to approximately calculate the energy and the relative intensity of the x-ray spectral components. Such theoretical predictions can simply be based upon one-electron integrals with the molecular orbital states described as linear combinations of the *s*, *p*, and *d*

atomic orbital functions (LCAO approximation). The calculated eigenvectors are used to obtain the dipole transition probabilities. From such MO calculations the relative amounts of *s*, *p*, and *d* contribution can readily be estimated.

In an earlier work, Henke and Smith¹ were able to demonstrate the feasibility of obtaining the $L_{II,III}$ spectra of phosphorous, sulfur, and chlorine in different chemical states by applying spectrographic techniques of such efficiency as to minimize the effects of radiation decomposition. Recently, the S- $L_{II,III}$ spectra have been more precisely measured and analyzed by Henke and Taniguchi^{2,3} for the SO_3^{2-} and SO_4^{2-} ions for polycrystalline samples and for the molecules containing single sulfur atoms and in the gas or vapor states— H_2S , SO_2 , SF_6 , $\text{C}_4\text{H}_4\text{S}$. The molecular orbital information derived from these spectra were compared to that obtained from the complementary photoelectron and K_α spectroscopy and to the predictions of molecular orbital theory. In this present work, the Cl- $L_{II,III}$ spectra for the ClO_2^- , ClO_3^- , and ClO_4^- ions for polycrystalline samples are measured, analyzed and compared to the photoelectron, K_α and MO calculated⁴ data for the same ionic systems. Also, important comparisons with the measured atomic $L_{II,III}$ spectra for Ar and NaCl are presented.

A striking difference in the experimental determinations of the $L_{II,III}$ spectra of the sulfur and the chlorine compounds has been that the latter undergo considerably greater chemical change as induced by the excitation radiation that is required for the spectral measurement. That radiation decomposition might be important in the soft x-ray spectra of chloro-anions had been discussed by Best⁵ in the electron excitation of Cl K_α spectra and had also been suggested by Urch⁶ in attempting to interpret the early spectra of Henke and Smith.¹ Subsequently, both Prins⁷ in x-ray photoelectron experiments and Sadovskii *et al.*⁸ in measuring Cl- $L_{II,III}$ emission

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SOME RECENT WORK IN LOW ENERGY X-RAY PHYSICS*

B. L. Henke

Abstract

1. X-Ray Sources--High intensity, monochromatic excitation sources are essential for quantitative studies of the emission processes for photoelectrons, Auger and secondary electrons and for fluorescent x-rays. Such sources are also needed for the calibration of the detectors and analyzers employed for these studies and for subsequent applications. In the low-energy x-ray region (10-100 Å/100-1000 eV) the direct radiation from an x-ray tube anode, with the appropriate filter and anode voltage, may be sufficiently monochromatic because the line radiation often dominates the associated continuum radiation. The line-continuum profiles have been measured and will be presented here for several useful K, L, and M characteristic line sources in order to illustrate the effect of filters and anode voltage. The absolute brightness of these sources (in photon/sec-stereadian) will also be presented.

2. Electron Spectroscopy--The electron spectroscopy of x-ray produced photoemissions has recently become an important tool in surface analysis. Photoelectron and Auger electron spectroscopy most effectively probe core electron states and the secondary electron spectroscopy probes the valence electron band states of the surface material. The basic processes that determine the photoemission spectra are the excitation, transport and the escape processes. In order that electron spectroscopy can be fully realized as a quantitative tool, considerably more must be known of the physics of these processes. This is particularly the case for secondary electron emission which is the most complex and for which there is no complete theory at this time.

Theoretical model results will be presented here along with examples of recently measured secondary electron energy distributions of metals and dielectrics. The secondary emission spectra rise sharply from zero electron kinetic energy to a peak value of about one eV and with a FWHM usually in the two to five eV region. These are being measured with a resolution of .04 eV using a hemispherical electrostatic analyzer. A uniform pre-acceleration field is employed which permits the application of a simple and accurate correction for a change in electron optical brightness associated with preacceleration (acceptance energy of the spectrograph is set at 15 volts).

It is hoped that measurements as these will also be helpful in gaining a more complete understanding of the secondary electron contrast dependence upon the surface state in scanning electron microscopy, and in the choice of x-ray photocathode materials particularly as used for pulsed x-ray measurements for temporal resolutions in the picosecond region.

3. X-Ray Spectroscopy--The low energy x-ray spectroscopy has been demonstrated to be a very useful tool for light element analysis, valence band and molecular orbital analysis, and for high temperature plasma diagnostics. The light elements emit only in the long wavelength x-ray region. Spectra from all elements involving transitions from the valence or molecular orbital levels to the nearby, relatively sharp core levels are in the one-to-several hundred eV region and do sensitively portray important outer electronic state structure. Plasma in the ten-million degree range (astrophysical and CTR, for example) emit most strongly in the low energy x-ray region. To accomplish this type of x-ray spectroscopy, the simpler and higher efficiency crystal spectroscopy is sometimes more appropriate than the grating spectroscopy even though the latter is inherently capable of higher resolution.

Presented here will be some examples of atomic and molecular, fluorescent spectroscopy of gaseous and solid samples using the multilayer analyzer (Langmuir-Blodgett type). The measured reflection coefficients and resolution for the lead myristate crystal will be presented in detail. And a simple method for unfolding the spectrographic lines and for decomposing overlapping spectra in order to gain spectral resolutions in the 0.5 eV range will be described.

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TECHNICAL REPORT -- MARCH 1978

MODELS AND MEASUREMENT FOR THE RESPONSE
OF DIELECTRIC X-RAY PHOTOCATHODES

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ABSTRACT

Most of the electrons which are ejected from a solid that is exposed to an x-ray beam appear as secondary electrons with kinetic energies less than 10 eV and with a relatively sharp energy distribution of FWHM values less than 5 eV. This secondary electron "signal" can be the basis for the measurement of the intensity and the temporal history (into the picosecond range) of pulsed x-ray sources. For example, x-ray photocathodes are currently applied in diode detectors and in streak and framing cameras. Simple models have been developed for the prediction of the shape and for the yield of the secondary electron distribution as these depend upon the x-ray photon energy and upon the x-ray absorption and solid state characteristics of the photocathode. To test these models, the secondary electron distributions and relative quantum yields have been measured for selected photocathode materials (semiconductors and insulators). Several alkali halides have been found to have much higher quantum yields and appreciably narrower energy distributions than do metal photocathodes, such as aluminum and gold for the x-ray photon energy region of 0.1 to 10 keV. The shape of the secondary electron distributions are essentially independent of photon energies in this region. The experimental results have been found to be in good agreement generally with the model predictions.

The Secondary Electron Emission Photocathode Characteristics for Time Resolved X-Ray Spectroscopy

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Recently the secondary electron energy distributions and the relative secondary electron yields for the 0.1 to 10 keV photon excitation region have been measured for gold, aluminum and for sixteen representative semiconductors and insulators (alkali halides), and a simple phenomenological model for X-ray photoemission has been developed. This work is discussed here as it might be applied to the application of streak cameras for time resolved X-ray spectroscopy.

§1. Introduction

Time resolved X-ray spectroscopy has recently become of considerable value in studies of high temperature plasmas in the one second range (magnetically confined fusion) to the picosecond range (laser produced fusion). Mode-locked laser systems are available that can generate high intensity pulses of X-radiation from matter in the picosecond region. Ultra-fast spectroscopy is needed for the characterization of such X-ray sources and of the effects of their radiation bursts upon measurement of the lifetimes of metastable atomic and molecular states and of certain photochemical processes.¹⁻³⁾

A proven method for accomplishing time resolved X-ray spectroscopy is that with the X-ray streak tube.⁴⁻⁶⁾ An X-ray beam is dispersed according to its photon energy along a slit-defined photocathode using a non-focusing crystal or a diffraction grating (or by a series of absorption filter and/or total-reflection monochromator channels). The secondary electrons from this slit source are used to form a line image at an image intensifier (needed particularly for ultra-fast spectroscopy). This line image is "streaked" to establish a time base using a pair of deflecting plates. The optical output of the image intensifier is recorded photographically. A schematic of such an X-ray streak tube is shown in Fig. 1. As indicated here, two types of imaging can be used, either an electron lens system^{7,8)} or a simple, proximity-focusing microchannel plate system.^{9,10)}

The intensity-and-photon-energy response

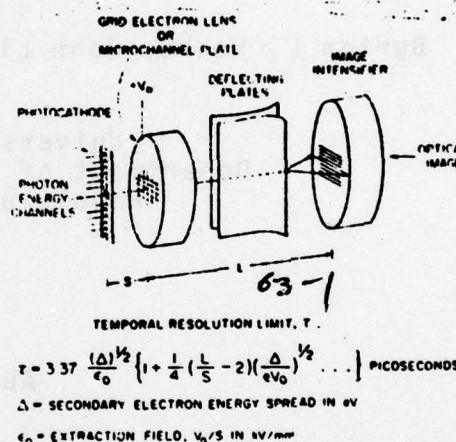


Fig. 1. Schematic of an X-ray streak tube as applied for time resolved X-ray spectroscopy. The temporal resolution limit, τ , is the difference in arrival time at the image intensifier for axially emitted electrons from the photocathode of initial velocities equal to zero and to v_0 . The corresponding energy spread, Δ , of the secondary electron emission is $1/2mv_0^2$.

and the temporal resolution of the streak camera are ultimately determined by the characteristics of the photocathode. In the sections that follow, we have attempted to review (1) the basic relationship between the photoemission and the electron-optical characteristics of the X-ray streak tube, and (2) the experimental and theoretical determination of the relevant photoemission properties of metal and dielectric X-ray photocathodes as have been recently investigated in this laboratory.¹¹⁻¹³⁾

§2. Some Basic Electron-Optical Relations

The number of secondary electrons per

C-K and Cl-L Emission Spectra and Molecular Orbital Analysis of CCl_4

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The C-K and $\text{Cl-L}_{\text{II,III}}$ low energy X-ray spectra from solid CCl_4 have been obtained using monoenergetic X-ray excitation and a lead myristate multilayer analyzing crystal. The Cl-L spectra was also measured in the vapor phase and compared with that measured in the solid phase. The deconvolved C-K and $\text{Cl-L}_{\text{II,III}}$ spectra are compared with the available Cl-K , and UPS spectra and with the results of CNDO/2, MINDO/3 and extended Hückel MO calculations.

§1. Introduction

The X-ray emission spectra from gaseous chlorinated methane derivatives have been previously reported by many authors. LaVilla and Deslattes¹⁾ studied the chlorine-K α emission spectra and Ehlert and Mattson²⁾ reported the carbon-K and chlorine-L spectra from four chlorinated derivatives of methane. The photoelectron spectra of chloromethanes were measured by Potts *et al.*³⁾ using 21 eV and 40 eV excitations and by Turner *et al.*⁴⁾ using 21 eV excitation. The experimental photoelectron spectra are in good agreement. Hopfgarten and Manne⁵⁾ provided a molecular orbital interpretation of available photoelectron and X-ray emission spectra of chloromethanes on the basis of the extended Hückel molecular orbital calculations.

In this laboratory,^{6,7)} the C-K and Cl-L emission spectra of CCl_4 and CHCl_3 and the C-K emission spectra of CH_4 were measured in the solid phase. The C-K emission spectra of methane and the Cl-L emission spectra of chloromethanes were also measured in the gas phase. Molecular orbital analysis of these chloromethanes were based upon the CNDO/2 and MINDO/3 SCF-MO calculations and upon results of available extended Hückel MO calculations.⁸⁾ As an example, the spectra and molecular orbital analysis of CCl_4 will be presented here.

§2. Experimental

Basic details of the experimental approach have been given elsewhere.^{7,8)} For high efficiency, an oxidized copper excitation source was used to create the C-1s hole and a carbon excitation source was used to create the Cl-2p hole. The X-ray tube was operated at 8 kV and 150 mA. A lead myristate multilayer⁹⁾ was used as the analyzer. A "pressure tuned"⁹⁾ constant flow proportional counter filled with propane at subatmospheric pressure was used as the detector.

In measuring the chlorine- $\text{L}_{\text{II,III}}$ spectra in the vapor phase, the sample pressure in the gas cell was maintained at one Torr for maximum intensity.¹⁰⁾ The chlorine- $\text{L}_{\text{II,III}}$ spectra of CCl_4 in the solid and vapor phases were measured under the same excitation and are presented in Fig. 1. As seen from Fig. 1, there are no substantial differences between the gas phase and solid phase spectra. Since the fluorescent intensity from the solid phase was about ten times higher than in the gas phase, the spectra from the solid samples were used in the detailed analysis presented here.

Reagent grade CCl_4 was obtained commercially with better than 99% purity. All of the spectra presented in this work are the sum of at least three repeated runs and the individual runs reproduced within statistical deviations. Over 10^4 counts were collected at the peak in all spectra and the spectrometer was calibrated using Rh, Mo and Nb M γ lines.^{7,8)} In all of the spectra, the peak intensities were normalized and background was not subtracted from the data because it was negligibly small.

A step-scanned spectrum thus obtained was

^{*}In partial fulfillment of PhD, University of Hawaii, May 1978.

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SOFT X-RAY INDUCED SECONDARY ELECTRON EMISSION
FROM SEMICONDUCTORS AND INSULATORS: MODELS AND MEASUREMENT

Burton L. Henke, John Liesegang*
and Steven D. Smith

Abstract

Secondary electron energy distribution curves (EDC's) and the total secondary electron yields relative to such for gold have been measured for seven semiconductors for which electron-electron scattering losses within the emitter were considered dominant and for nine insulators (alkali halides) for which electron-phonon scattering losses were expected to be dominant in the transport process. The secondary electron spectra were excited by Al-K α (1487 eV) photons and were measured from evaporated dielectric films (of about 0.3 micron thickness) on conducting substrates with an electrostatic, hemispherical analyzer of about .03 eV resolution. Some of the dielectric photoemitters have appreciably narrower energy distributions and higher yields than has gold; CuI and CsI have EDC widths at half-maximum of about one-third of that for gold, and yield values of eleven and thirty times greater. The FWHM and secondary electron yield for gold were measured to be about 4 eV and .05 electrons per normally incident photon, respectively. The shapes of the EDC's were found to be essentially unchanged for photon excitation in the 0.1 to 10 keV region. Strong structural features appear only in the alkali halide EDC's and it is proposed that these are mainly the result of single electron promotion of secondaries from the valence band by plasmon de-excitation. A relatively simple model for x-ray photoemission has been developed which assumes that direct excitation of secondaries by photoelectron and Auger electron "primaries" is the dominant excitation mechanism and accounts for both electron-electron and electron-phonon scattering in the transport process. Free-electron conduction band descriptions are assumed. The theoretical and experimental curves are in satisfactory agreement.

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LOW ENERGY X-RAY EMISSION SPECTRA AND
MOLECULAR ORBITAL ANALYSIS OF CH_4 , CCl_4 AND CHCl_3

Rupert C. C. Perera* and Burton L. Henke

Abstract

The C-K and Cl-L_{II,III} low energy x-ray spectra from solid CCl_4 , CHCl_3 and the C-K x-ray spectrum from solid CH_4 have been obtained using monoenergetic x-ray excitation and a lead myristate multilayer analyzing crystal. The C-K spectrum of methane and Cl-L_{II,III} spectra of the chloromethanes were also measured in the gas/vapor phase and compared with those measured in the solid phase. The deconvolved spectral components are aligned on a common energy scale with the complementary x-ray emission and photoelectron spectra by identifying the same molecular orbital in all spectra. Such an alignment procedure yields a C-1s ionization energy of gaseous CH_4 , and solid CCl_4 and CHCl_3 as 290.0 eV, 293.5 eV and 293.1 eV, respectively; and the Cl-2p_{3/2} ionization energy of solid CCl_4 and CHCl_3 as 206.5 eV and 204.8 eV. Results of the CNDO/2 and MINDO/3 MO calculations have been presented and compared with the available results of the extended Huckel MO method and with the deconvolved spectral components. From the geometry program in the MINDO/3 MO calculations, the C-H bond length in CH_4 is 1.102 Å, the C-Cl bond length in CCl_4 is 1.751 Å, and the C-H and C-Cl bond lengths in CHCl_3 are 1.100 Å and 1.744 Å, respectively. Comparison with the vapor/gas phase spectra shows essentially the same energies for spectral components in the C-K and Cl-L spectra from CH_4 and CCl_4 , whereas the spectral components in the Cl-L spectra of CHCl_3 have energies in the gas phase that are significantly higher than those for the solid phase.

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PHYSICS AND APPLICATION OF MULTILAYER "CRYSTALS" FOR SPECTRAL ANALYSIS IN THE 50-100 Å REGION. Burton L. Henke, University of Hawaii, Honolulu, Hawaii 96822.--Insoluble monomolecular layers on a water surface (e.g., lead salts of fatty acids) are successively deposited upon a glass substrate as Langmuir-Blodgett multilayer "crystals" and applied as efficient analyzers for low-energy x-radiations in the 100-200 eV region with energy resolutions of about one eV. A simple structural model for the salts of the straight-chain fatty acids has been used with both the mosaic and the Darwin-Prins crystal theories in order to develop semi-empirical expressions for the multilayer analyzer efficiency and resolution as a function of wavelength.

By a straightforward extension of flat-crystal vacuum fluorescence spectroscopy, the molecular orbital L_{II,III} spectra have been measured for phosphorous, sulfur and chlorine in their several oxidation states. These spectra, along with such from K_β, uv and x-ray photoelectron spectroscopy, have permitted a complete determination of the relative s, p and d character of the molecular orbitals.

The multilayer analyzers have also been applied to the low-energy x-ray spectral analysis of high temperature plasmas as generated by pulsed laser and electron beams. For pulsed sources, non-focussing crystal geometries such as convex-cylindrical are employed. Such spectral measurements yield the density and temperature of the plasma. By coupling these multilayer analyzers onto streak cameras, time-resolved spectroscopy into the picosecond region should be attainable in this low-energy x-ray region.

- a) Burton L. Henke
Ph. (808) 948-7660
- b) Low energy x-ray analysis by crystal spectroscopy.
- c) Oral Presentation.
For Applied Crystallography Group Invited Paper
- d) 35 mm slide projector

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) <p>The work accomplished in this grant period has been directed particularly to the development of low energy x-ray and electron spectroscopy for application to high temperature plasma diagnostics which is of considerable importance in controlled thermonuclear fusion research at this time. Optimized, high-efficiency crystal spectroscopy has been developed for the 100 to 500 eV photon energy region, using improved long-spacing multilayer analyzers constructed in this laboratory of 2d-values in the 80-160 A range. (cont.)</p>		

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of flat or curved geometry and for dc or pulsed x-ray sources. The dc spectroscopy has been demonstrated in this laboratory as applied to the measurement of valence band and molecular orbital energies of selected compounds in both the solid and gas states and with spectral resolutions, using specially developed deconvolution methods, of a few tenths of an electron volt. The fluorescent lines that are measured result from transition of valence electrons into the nearest, relatively sharp core levels with photon energies typically in the 100 eV region for all elements. The measured values have been found to agree well with molecular orbital calculations using methods such as the CNDO, MINDO and ab initio, performed here and in other laboratories. These measurements are also in good agreement with those of the complementary uv and x-ray excited photoelectron spectroscopy. In order to achieve time-resolved spectroscopy into the picosecond region (as needed for laser fusion studies) the x-ray spectrum is dispersed along a transmission x-ray photocathode slit and the converted secondary electrons are focussed and deflected across the face of an image intensifier section of an x-ray streak or framing camera. For this application, the photocathode must present a secondary electron energy distribution of width of about one eV or less and with high quantum efficiency. A program has been established in this laboratory on the development of theoretical models and of the precise experimental measurement of the total and secondary electron quantum yields and of the secondary electron energy distribution functions for both metals and dielectrics. High resolution (<.05 eV) secondary electron energy distributions have been measured for gold, aluminum, and for sixteen semiconductors and insulators (alkali halides). New model expressions for these distributions have been derived which are in good agreement with the experimental results. A new facility has been completed for the absolute measurement of the total and secondary electron yields of both thick and transmission x-ray photocathode systems utilizing selected filtered, fluorescent line sources of photon energy in the 0.1 to 10 keV region. First page abstracts of published papers that describe these research results are presented here.

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